

## **Hydrogen Production by Steam Reforming of Bio-Oil Aqueous Fraction over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst**

C.-F. Yan, F.-F. Cheng, R.-R. Hu

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 3: Hydrogen Production Technologies - Part 2

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-3

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-653-8

# Hydrogen Production by Steam Reforming of Bio-Oil Aqueous Fraction over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> Catalyst

**Chang-Feng Yan, Fei-Fei Cheng, Rong-Rong Hu**, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China

## Abstract

Two kinds of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts were prepared by impregnation method or by co-precipitation method. A laboratory scale fixed-bed reactor was employed to investigate the catalyst performance in hydrogen production by steam reforming bio-oil aqueous fraction. Effects of reaction temperature, and the different preparation methods of the catalyst on the hydrogen production performance of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts were examined. The obtained results were compared with commercial nickel-based catalysts (Z417). Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst by co-precipitation method showed the best catalytic performances. At W/B=4.9, T=800 °C, H<sub>2</sub> yield reaches the highest of 72.9 % and H<sub>2</sub> content of 70.0 % were obtained., these values were higher than Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts were prepared by impregnation method and commercial nickel-based catalysts (Z417).

## 1 Introduction

Hydrogen is an emerging new energy carrier with significantly environmental impact as its combustion is clean of pollutants. Most hydrogen now is generated from fossil fuels such as natural gas, naphtha, heavy oil and coal via catalytic reforming and partial oxidation processes [1]. Due to environmental pollution and the high dependence on fossil fuels, the world-wide interest in the energy area is focused on the production of hydrogen from alternative fuels. Biomass has been proposed as an alternative feedstock for hydrogen production not only because it is renewable but also because it is a CO<sub>2</sub> neutral energy supply [2]. Hydrogen can be generated from biomass mainly via two kinds of thermochemical processes, the gasification [3-4] or the flash pyrolysis [5-7] followed by steam reforming of the pyrolysis oil.

Recently, more attention has been paid to bio-oil aqueous fraction steam reforming and a few catalysts have been investigated, for example, UC G-90C [8-10], ICI 46-1[8,9], Ni-Al [11], Pt, Rh and Pt based catalyst [12] and so on. The aim of the present work is to investigate the catalyst Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> performance in hydrogen production by steam reforming bio-oil aqueous fraction and compare it with commercial nickel-based catalysts (Z417). Effects of reaction temperature and different preparation methods of the catalyst on the hydrogen yield and hydrogen selectivity is evaluated.

## 2 Experimental

### 2.1 Catalyst preparation

Two kinds of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts were prepared impregnation method or co-precipitation method respectively. Firstly, The catalysts precursors were prepared by adding aqueous solution of ZrOCl<sub>2</sub> or aqueous mixture solution of metals, ZrOCl<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, which was depended on the catalyst component, to a vigorously stirred solution of NH<sub>4</sub>OH at 50 °C. The resulted precipitate was filtered and washed with distilled water, then dried in air at 110 °C for 6 h. Finally, the support precursor was calcined in air at 600 °C for 6 h. Then, Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts were prepared by impregnating ZrO<sub>2</sub> (CeO<sub>2</sub>-ZrO<sub>2</sub>) powder with Ni(NO<sub>3</sub>) and Ce(NO<sub>3</sub>)<sub>3</sub> (Ni(NO<sub>3</sub>)), as Ni and Ce precursor, followed by drying at 110 °C for 12 h, calcinating at 800 °C for 6 h and natural cooling for testing.

### 2.2 Apparatus and steam reforming tests

The bio-oil aqueous fraction steam reforming experiments were carried out in a continuous flowing system using a fixed-bed reactor made of quartz under atmospheric pressure. The catalyst powder was placed in the middle of the quartz tube, which was heated by the furnace equipped with temperature controller. The calcined catalyst was reduced in situ in 5 % H<sub>2</sub>/N<sub>2</sub> stream at 700 °C for 4 h prior to use. Bio-oil aqueous fraction was fed into the reactor at a constant rate by a peristaltic pump. The product gas exiting from the reactor was cooled and dried before entering gas chromatograph (GC522) for analysis. At the end of the catalytic tests, the catalyst was cooled under N<sub>2</sub> stream.

The bio-oil aqueous fraction steam reforming performance over a given catalyst was studied by measuring hydrogen yield efficiency and the content of product gas. Hydrogen yield efficiency was denoted as Y<sub>H<sub>2</sub></sub>, the content of product gas (hydrogen, carbon dioxide, methane, carbon monoxide) was denoted as Vol%product. Since nitrogen was introduced as carrier gas, measured value of gas component was normalized. Hydrogen content was defined in terms of the moles of hydrogen in per mole of product gas:

$$V\%_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \times 100\% \quad (4)$$

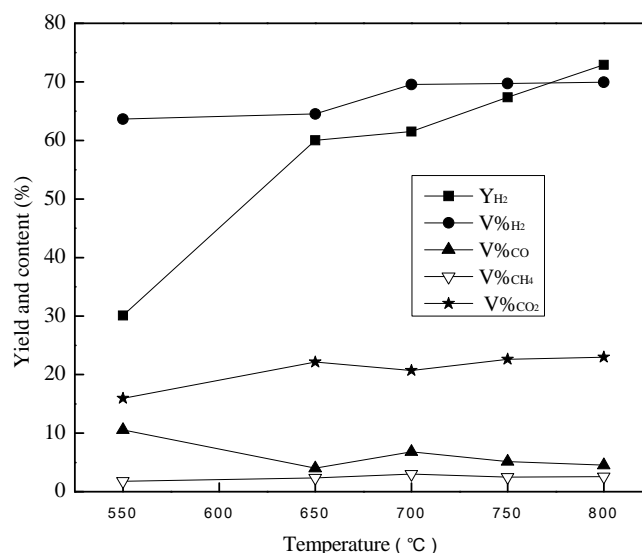
The calculated method of the content of other product gas was similar to that of H<sub>2</sub>.

According to the reaction (3), the stoichiometric H<sub>2</sub> is calculated. Then hydrogen yield efficiency (Y<sub>H<sub>2</sub></sub>) is calculated as follow:

$$Y_{H_2} = \frac{H_2 \text{ yield}}{\text{stoichiometric } H_2} \times 100\% \quad (5)$$

### 3 Results and discussion

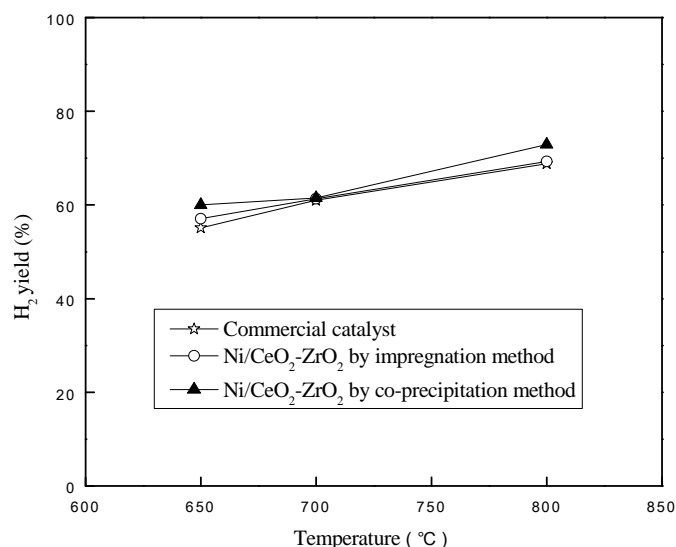
#### 3.1 Effects of reaction temperature



**Figure1: Effects of reaction temperature on the hydrogen yield and the content of the product gas (Catalyst: Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (12 wt% Ni, 7.5 wt% Ce) by co-precipitation method; W/B=7.7).**

Fig. 1 presented the effects of reaction temperature on the reforming reaction under the reaction temperature ranging from 550 °C to 800 °C. It could be found that reaction temperature had significant effects on hydrogen yield and content of the product gas. The hydrogen yield increased obviously with the reaction temperature increasing. At 550 °C, the hydrogen yield was just 30.1 %, but it reached the highest of 72.9 % with the reaction temperature increase to 800 °C. In the shown reaction temperature range, CO content and CO<sub>2</sub> content presented on the contrary current, and CO content reached the maximum value of 10.6 %, but CO<sub>2</sub> content arrived at the minimum value of 16.0 % at 550 °C respectively. This may be attributed to the fact that the reverse water gas shift (RWGS) reaction occurred. Aupretre et al. [13] pointed out that CO was generated from RWGS reaction in the steam reforming ethanol as well. H<sub>2</sub> content increased obviously as the reaction temperature increase, and reached the maximum value of 69.9 % at 800 °C. CH<sub>4</sub> content first increased and then decreased. At 700 °C, a maximum CH<sub>4</sub> content of 3.0 % was obtained, the cause of which might be that the side reaction of methanation of CO<sub>2</sub> took place in the steam reforming process at this condition. Vannice [14] pointed out that Ni showed high activity in the methanation of CO<sub>2</sub>.

### 3.2 Comparison of two kinds of catalysts and commercial catalysts



**Figure 2: Comparison of H<sub>2</sub> yield between two kinds of self-prepared catalyst and commercial catalyst (Catalysts: Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (12 wt% Ni, 7.5 wt% Ce); W/B=7.7).**

Fig. 2 presented the hydrogen yield as a function of the reaction temperature for two kinds of self-prepared Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst and commercial nickel-based catalysts (Z417). As the reaction temperature increased from 650 °C to 800 °C, the hydrogen yields of three kinds of catalysts increased. In the given reaction temperature range, the hydrogen yields of self-prepared catalysts were higher than that of commercial catalysts, which indicated that self-prepared catalysts had better catalytic activities. Table 1 showed that the effects of three kinds of different catalysts on content of the product gas at the same conditions (T=650 °C, W/B=7.7). The H<sub>2</sub> and CO<sub>2</sub> contents got via catalyst by co-precipitation method was higher than the other catalysts, on contrast, the content of CO and CH<sub>4</sub> were lower. Hence, from hydrogen yield and content point of view, Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst by co-precipitation method had better catalytic performance than Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst by impregnation method and commercial nickel-based catalysts (Z417).

**Table 1: Comparison of the content of the product gas between self-made catalyst and commercial catalyst.**

Catalysts	V% <sub>H<sub>2</sub></sub>	V% <sub>CO</sub>	V% <sub>CH<sub>4</sub></sub>	V% <sub>CO<sub>2</sub></sub>
Commercial catalyst Z417	64.0	5.3	2.0	21.7
Ni/CeO <sub>2</sub> -ZrO <sub>2</sub> by impregnation method	63.3	9.1	2.3	18.3
Ni/CeO <sub>2</sub> -ZrO <sub>2</sub> by co-precipitation method	64.5	4.0	2.3	22.1

Catalysts: Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (12 wt% Ni, 7.5 wt% Ce); W/B=4.9; T=650 °C

## 4 Conclusions

Based on the present results, we could find that Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts by co-precipitation method had higher catalytic activity for hydrogen production from the steam reforming of the bio-oil aqueous fraction. Reaction temperature had significant effects on hydrogen yield and content of the product gas. At T=800 °C and W/B=7.7, the hydrogen yield and content of the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst by co-precipitation method reached the maximum value of 72.9 % and 70.0 % respectively in the range of experimental temperature, which were higher than those of Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst by impregnation method and commercial nickel-based catalysts (Z417). Thus, it was a promising catalyst for hydrogen production from bio-oil aqueous fraction steam reforming.

## References

- [1] M.A. Pefia, J.P. Gomez, J.L.G. Fierro, Appl. Catal. A: Gen. 144 (1996) 7-57.
- [2] E.Ch. Vagia, A.A. Lemonidou, Appl. Catal. A: Gen. 351 (2008) 111-121.
- [3] J. Schoeters, K. Maniatis, A. Buekens, Biomass 19 (1989) 129-143.
- [4] D. Sutton, B. Kelleher, J.R.H. Ross, Fuel Proces. Technol. 73 (2001) 155-173.
- [5] A.A. Lappas, M.C. Samolada, D.K. Latridis, S.S. Voutetakis, I.A. Vasalos, Fuel 81 (2002) 2087-2095.
- [6] D. Mohan, C.U. Pittman Jr., P.H. Steele, Energy Fuels 20 (2006) 848-889.
- [7] Z. Qi, C. Jie, W. Tiejun, X. Ying, Energy Cov. Manage. 48 (2007) 87-92.
- [8] D. Wang, S. Czernik, D. Montane, M. Mann, E. Chornet, Ind. Eng. Chem. Res. 36 (1997)1507.
- [9] M. Marquovich, S. Czernik, E. Chornet, D. Montane, Energy Fuels 13 (1999) 1160.
- [10] D. Wang, D. Montane, E. Chornet, Appl. Catal. A: Gen. 143 (1996) 245.
- [11] J. R. Galdamez, L. Garcia, R. Bilbao, Energy Fuels 19 (2005) 1133.
- [12] C. Rioche, S. Kulkarni, F. C. Meunier, J. P. Breen, R. Burch, Appl. Catal. E: Environ. 61 (2005) 130.
- [13] F. Aupretre, C. Descorme, D. Duprez, Catal. Commun. 3 (2002)263-267.
- [14] M.A. Vannice, J. Catal. 50 (1977) 288-295.